Design and Construction of a High-Pressure Cell for Use In X-ray Diffraction[1]

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ABSTRACT

This work describes the setup and operation of a high-pressure cell used in powder X-ray diffraction. Because the most current hydrate XRD measurements have been performed at low temperatures to ensure hydrate stability at atmospheric pressure, extrapolation has been required to determine hydrate structure at *in situ* conditions. With high-pressure capabilities, however, this system can extend current structural knowledge without extrapolation, leading to less error in predictive modeling and a more accurate view of *in situ* hydrates. The cell has both low and high-temperature capabilities, operating from 77 to 300K using liquid nitrogen boil-off as a means of refrigeration, and can maintain pressures from 14kPa to 7 MPa.

Preliminary measurements of carbon dioxide hydrates at *in situ* conditions have been taken, and lattice parameters are comparable to those in the literature.

KEY WORDS: diffraction, hydrates, in situ, X-ray

1. Introduction

Previous studies of hydrate structure using X-ray diffraction (XRD) have been performed at very cold temperatures: as low as 173 K to ensure hydrate stability at atmospheric pressure. While valid, these measurements do not accurately simulate *in situ* hydrate conditions, possibly leading to erroneous results when models are extrapolated to higher formation temperatures. Although neutron diffraction studies at elevated temperature and pressure conditions have been made, the availability of such equipment makes these results prohibitively expensive to acquire, and thus definitive *in situ* hydrate structural measurements using X-ray diffraction, a much cheaper method, are necessary [1,2].

In addition to the data extrapolation problems associated with the initial XRD cell, the previous design also allowed a substantial amount of condensation to accumulate on the surface of the sample being tested. Not only did this interfere with the overall quality of the patterns obtained, but condensation also limited the amount of structural information that could be acquired about the hydrates.

To solve the stated problems, an XRD cell was custom designed and built to replace the former equipment.

2. Design of the cell

Before construction, several requirements for operation of the cell were specified:

- It must able to contain a pressure of approximately 6.9 MPa to simulate *in situ* conditions
- It must allow for the passage of cobalt X-radiation
- It must contain enough sample surface area to give strong diffraction signals

Because the cell had to contain high pressures, single-bodied construction was necessary. Additionally, the material used had to allow X-ray transmission. Fortunately, beryllium (Be) is a material that is not only strong, but also transparent to X-rays, and thus was a suitable choice for the new cell [3, p. 466; 4].

To determine the dimensions of the beryllium cell, two factors had to be optimized: degree of X-ray attenuation and pressure holding capability. A thick-walled cell may contain higher pressures, but would reduce the intensity of the X-ray signal substantially. Conversely, a thin-walled cell would allow maximum X-ray transmission, but would not safely support the pressures required.

As shown in Figure 1, the X-rays are attenuated twice by passing in and out of the cell through the tube wall. Therefore, to get at least 30% (an arbitrary value) of the intensity compared to an open sample, we need:

$$\frac{I}{I_0} = e^{-\rho(\frac{\mu}{\rho})(2x)} = 0.3 \tag{1}$$

where I is the X-ray beam intensity with the beryllium tube, I_0 is the intensity with an open sample; ρ is the density, and (μ/ρ) is the mass absorption coefficient of Be; $2x$ is the total penetration thickness through Be by the X-rays. According to Cullity, the density of Be is 1.85 g/cm^3, the mass absorption coefficient is 2.42 cm^2/gm for cobalt radiation [3]. Based on these values, the maximum wall thickness allowed for the Be tube is 0.13cm (x). In the final design, we used a beryllium tube with a wall thickness 0.12cm to ensure a strong diffracted X-ray beam.

The desired experimental condition was to have stable methane hydrates at 277.15K, a typical seafloor temperature. This requires a minimum pressure in the cell of 3.86MPa [5]. However, to ensure high conversion and to keep hydrates stable over minor temperature fluctuations, greater pressures are required. Here we arbitrarily choose 6.9 MPa as the maximum working pressure.

Many factors, such as micro-defects within the beryllium and the strength of the joints between the beryllium and supporting materials affect the overall strength of the design. To ensure safe operation, a safety factor of 5 was considered based on suggestions from a professional designer, Ivan Getting, at the University of Colorado at Boulder. Thus a bursting pressure of the beryllium tube of 34.5MPa was required.

Assuming that the tube can be approximated as a thin wall tube, the maximum pressure can be calculated as:

$$p = \frac{\sigma x}{d} \tag{2}$$

Where p is the maximum pressure a thin wall tube can stand, σ is the yield tensile strength, x is the wall thickness and d is the radius of the tube [6]. With the maximum pressure, yield tensile strength and wall thickness known, the radius of the tube is then calculated as:

$$d = \frac{\sigma x}{p} = \frac{414\text{MPa} * 0.12\text{cm}}{34.5\text{MPa}} = 1.41\text{cm} \tag{3}$$

For manufacturing purposes, we chose 1.5cm as the inner diameter of the Be tube. This provides a safety factor of 4.7 when the working pressure is 6.9MPa.

3. Cell Assembly

In order to secure the Be tube to the Siemens D-500 diffractometer already in place, a stainless steel housing was constructed to support the tube and also provide places of Be tube attachment. Three flanges were attached to the tube (see figure 2): flange 1 fit the tube to the goniometer face of the diffractometer as well as accepted an inlet gas feed, flange 2

was placed at the opposite end of the tube to serve as a mounting plate for the pressure-sealing flange, and flange 3 allowed for the containment of pressure as well as temperature monitoring via a thermocouple feed-through. An O-ring groove was machined into flange 2 to ensure an effective seal against high pressures.

Flanges 1 and 2 were attached together via a stainless steel tube (not shown) with a 65° window removed on both sides to allow for X-rays to pass through the beryllium tube.

A sample holder containing the sample to be measured is inserted into the beryllium tube/stainless steel housing, and held in place by several pins and plungers. This system was used to ensure precise placement of the sample surface (a must for good diffraction work) each time a new sample was mounted. An overall view of the assembly can be seen in Figure 3.

In this system, temperature is regulated by passing gaseous nitrogen (from liquid nitrogen boil-off) over the beryllium enclosure. Constant flow of the dry, gaseous nitrogen ensured no condensation would occur on the outside of the beryllium tube, even at lower temperatures. A Proportional-Integral-Derivative (PID) controller, attached to the thermocouple of flange 3, regulates the heating of the boil-off by means of altering current flow to heating tape surrounding the cooling apparatus (not shown). Temperature control of the cell can be maintained from 78K to 300K, with fluctuations of approximately 1.5K.

4. Calibration and alignment

To ensure proper operation and correct alignment of the newly installed system, extensive calibration was required. In order to calibrate, a standard sample known as SRM 1976 obtained from the National Institute of Standards and Technology (NIST) was used. SRM 1976 is a flat plate approximately 5cm x 5cm made from alumina with peak intensities and positions given by NIST. For proper alignment in any diffraction system, both intensities and peak positions in a given pattern must match those of a known sample's pattern. To compare the patterns from the high-pressure system to those provided by NIST, the sample holder was retrofitted with a 1.4cm x 4.0cm piece of the SRM 1976, and diffraction work was performed. See Figure 4 for details of this design.

After substantial adjustments, alignment and calibration of the new system was achieved. For reproducibility, the diffraction work was performed three times on the sample. As shown in Figures 5a and 5b, the peak position differences between our results and those provided by International Center for Diffraction Data (ICDD, 82-1467) were less than 0.01^o. This difference is equivalent to 0.02% in actual lattice parameter measurements, and is well within the tolerance for excellent diffraction work.

5. Preliminary Measurements

Upon calibration, preliminary measurements using high-pressure CO_2 hydrates were made. Lattice parameters were calculated and compared to low temperature measurements obtained from the original cell. As shown in Figure 6, the high-pressure data taken at 275

and 276K agree very well with the low temperature thermal expansivity measurements. This demonstrates that the high-pressure cell is capable of measuring *in situ* hydrate properties.

6. Conclusions

A diffraction cell with high-pressure and low-temperature capabilities for conventional X-ray diffraction was designed. The central part of this design is a Be tube with 1.4cm I.D. and 0.12cm wall thickness. The working pressure of the Be tube was 6.9MPa with a safety factor of 4.7. Special supporting matters such as aligning tool and sample holder were also designed to accommodate the special shape of the cell. The hi-pressure low-temperature cell was aligned and calibrated. The average peak position difference between actual measurements and International Center for Diffraction Data database values were found to be less than 0.01^o. CO_2 hydrates were successfully formed in the high-pressure cell at 275 and 276K. *In situ* lattice parameters agreed well with low temperature measurements.

References

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Figure Captions

Fig. 1. Be tube and X-ray path

Fig. 2. Be tube with supporting materials

Fig. 3 The overall assembly of the cell

Fig. 4 Standard calibration material

Fig. 5a. Pattern obtained for SRM 1976 in high-pressure system

Fig. 5b. Difference between NIST data and new system measurements of SRM 1976

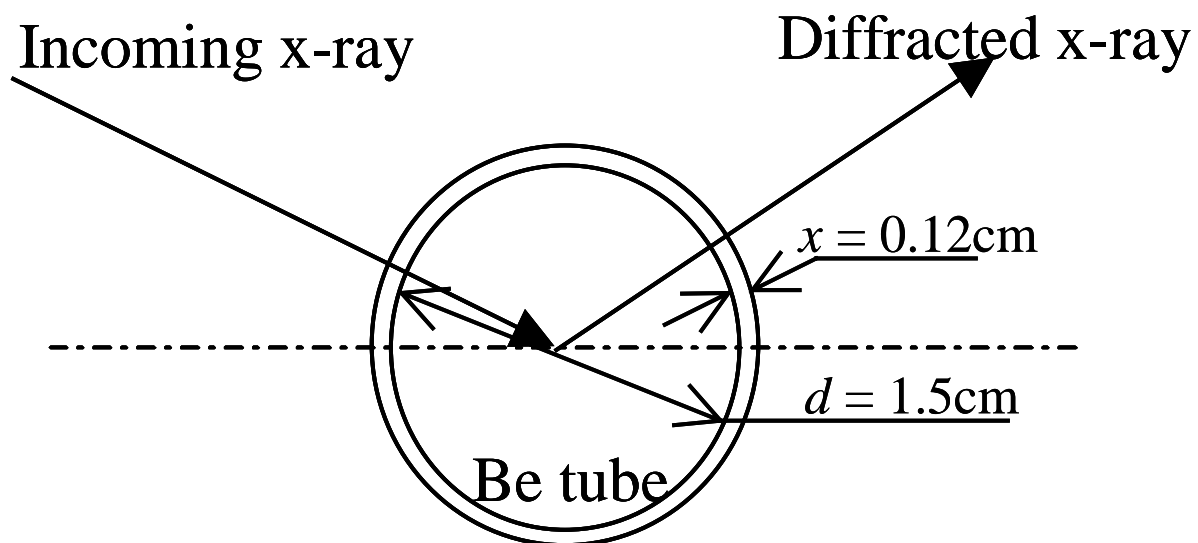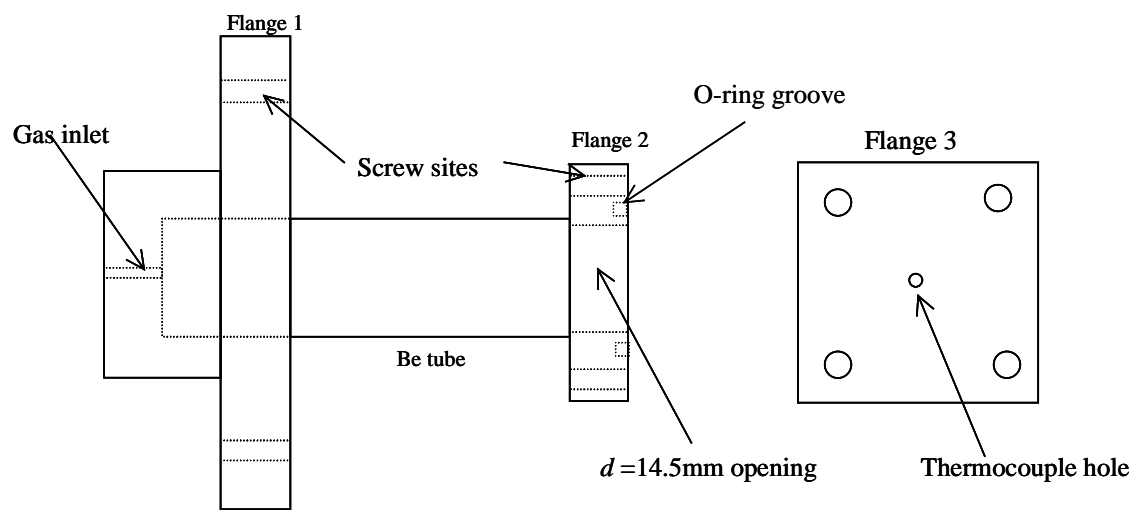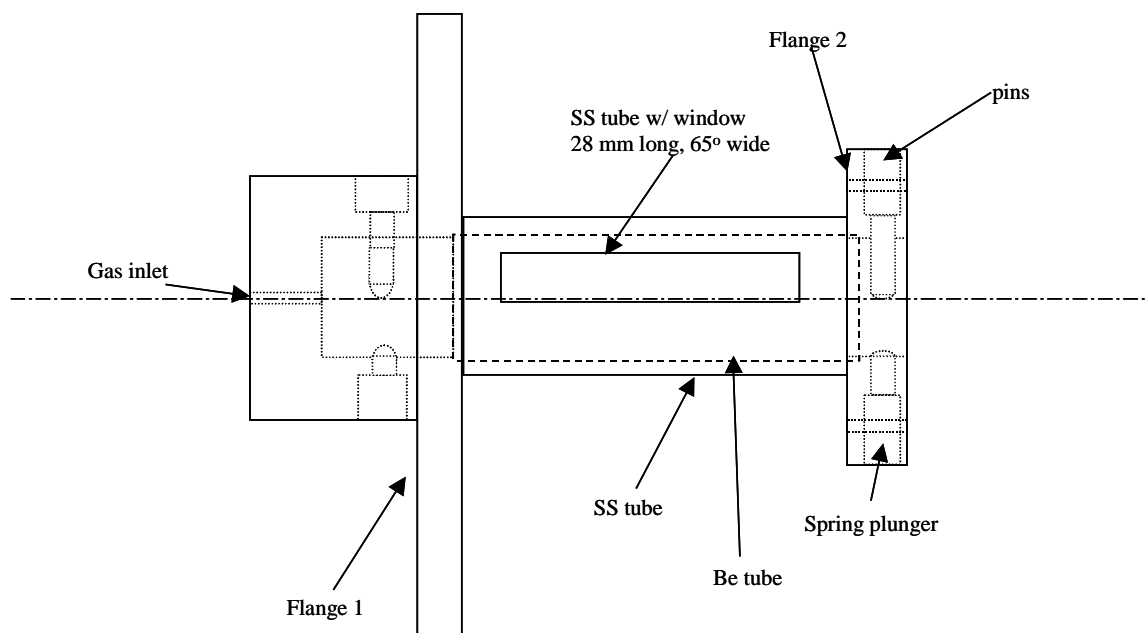**Fig. 6.** In situ measurements with high-p cell compared to low-T data

Incoming x-ray

Diffracted x-ray

$x = 0.12$cm

$d = 1.5$cm

Be tube

Fig. 1

Flange 1

Gas inlet

Screw sites

O-ring groove

Flange 2

Flange 3

Be tube

$d = 14.5$mm opening

Thermocouple hole

Fig. 2

Flange 2

pins

SS tube w/ window
28 mm long, 65° wide
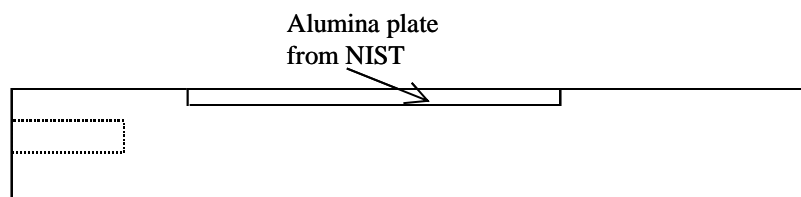
Gas inlet

SS tube

Be tube

Spring plunger

Flange 1

Fig. 3

Alumina plate
from NIST

Fig. 4

Fig. 5a

Fig. 5b

Fig. 6